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Publication date:
2016

Document Version
Publisher's PDF, also known as Version of record

Graphene Supported Au-Pt Core-Shell Catalyst: Electrocatalysis of Formic Acid Oxidation

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Introduction

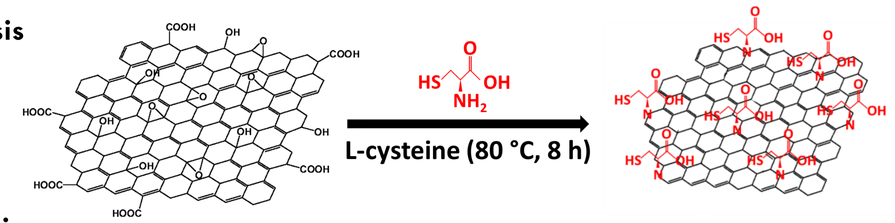
Polymer electrolyte membrane fuel cell (PEMFC) is energy technology limited by the need for expensive catalysts, such as Pt.[1] Highly active graphene-supported Au-Pt core-shell (Au@Pt) catalyst with atomically thin Pt shell and low Pt loading is here used in PEMFCs for formic acid (FA) oxidation. Commercial catalyst 20 % of Pt on graphitized carbon (C-$Pt_{20\%}$) was a reference in all experiments.

Key challenges:

1. Chemical syntheses of graphene-Au@Pt catalyst,
2. Electrocatalysis of FA oxidation and oxygen reduction reactions (ORR),
3. Functional testing of graphene-Au@Pt in PEMFC.

Graphene-Au@Pt synthesis

1. Graphene synthesis



2. Au@Pt NP formation

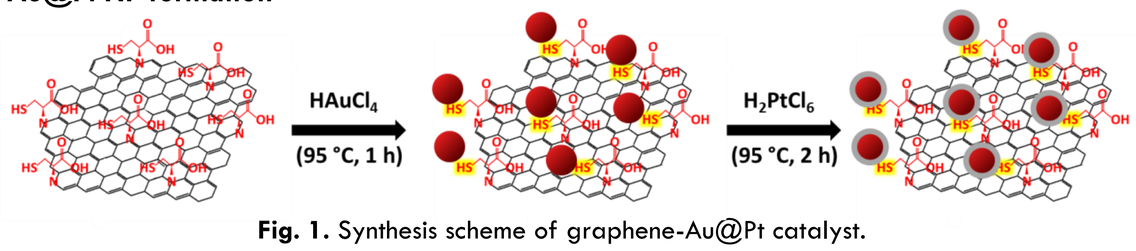


Fig. 1. Synthesis scheme of graphene-Au@Pt catalyst.

Graphene-Au@Pt synthesis (Fig. 1) starts by graphene oxide (GO) reduction to graphene and covalent (CYS-graphene) functionalization by L-cysteine (CYS). Au cores are formed next and strongly bonded to the CYS thiol group, followed by Pt shell formation. The Au:Pt precursors ratio corresponds to an atomically thin Pt shell on the Au cores.

Graphene-Au@Pt characterization

GO reduction to graphene was followed by UV-Vis spectroscopy: 235 and 303 nm peaks are converted to a 265 nm peak (Fig. 2a), and the Au NP plasmon peak (520 nm) is dampened by Pt shell formation.[2] X-ray photoelectron spectroscopy (XPS) confirms CYS–graphene bond types (pyrrolic N at 399.5 eV), Fig. 2b. Fig. 2c shows 2-ethanesulfonic acid (MES) on Au (167.98 eV) – a NP stabilizing agent, and strong covalent Au–thiol (163.2 eV) bonds which ensure catalyst stability.

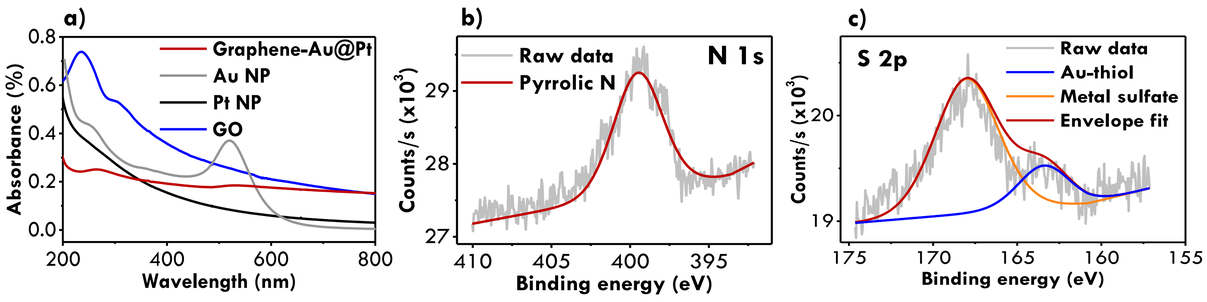
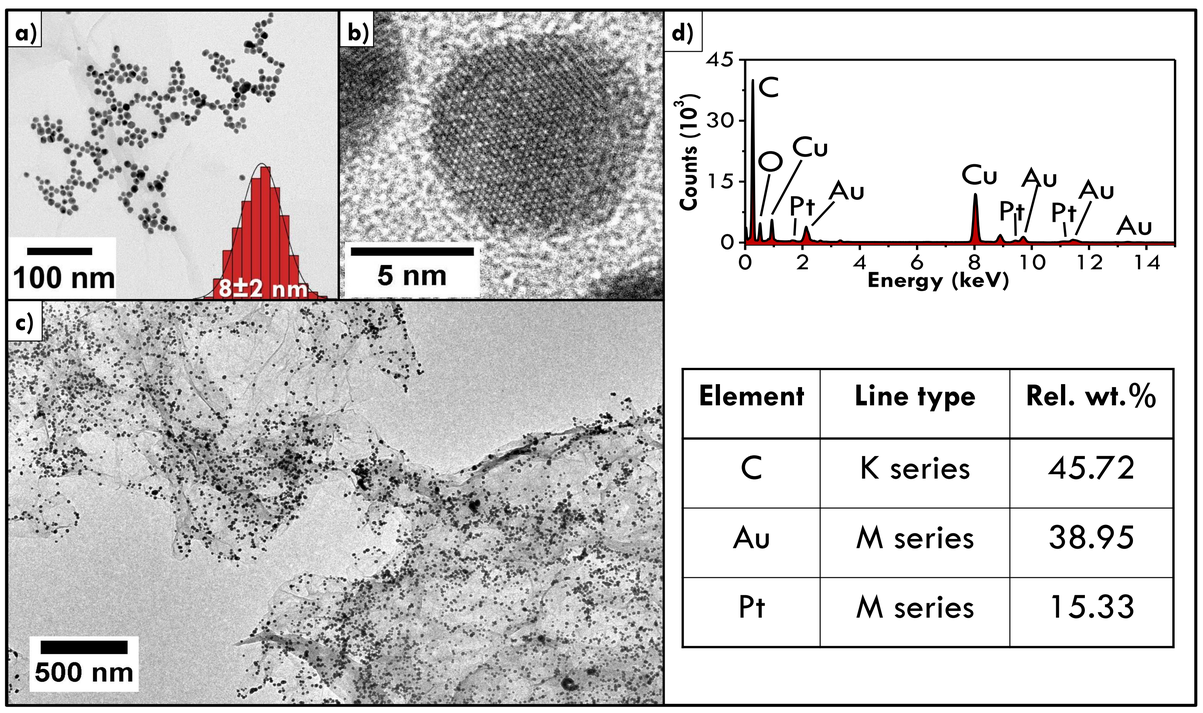


Fig. 2. Graphene-Au@Pt: **a)** UV-Vis component spectra; high-resolution XPS of **b)** N and **c)** S.

Au@Pt NPs of uniform size (8 ± 2 nm) was imaged by transmission electron microscope (TEM, Fig. 3. a, b). Homogeneous distribution of NPs on graphene (Fig. 3. c) is based on its high surface area and ensures good Au@Pt stability. Composition of the NPs was measured by energy-dispersive X-ray spectroscopy (EDX), from which atomic ratio Au:Pt = 2.76:1 can be obtained (Fig. 3c).



Element	Line type	Rel. wt.%
C	K series	45.72
Au	M series	38.95
Pt	M series	15.33

Fig. 3. a) Graphene-Au@Pt TEM image, inset is size distribution histogram. **b)** High resolution TEM image of a single Au@Pt on graphene. **c)** Overview TEM image of graphene-Au@Pt. **d)** Graphene-Au@Pt EDX spectra and C:Au:Pt relative weight ratio.

Electrocatalysis and PEMFC experiments

Electrocatalysis in half-cell experiments:

Fig. 4. shows higher Pt activity of graphene-Au@Pt NPs than of C-$Pt_{20\%}$ for FA oxidation (anode) and ORR (cathode). Both catalysts exhibited signal decay during cycling. However, graphene-Au@Pt (59th cycle) showed several times higher currents than C-$Pt_{20\%}$ (58th cycle) in FA oxidation (Fig. 4b) and 69.4 mV lower overpotential towards ORR than C-$Pt_{20\%}$ (Fig. 4c).

Anode, FA oxidation: $HCOOH \rightarrow CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$

Cathode, ORR: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

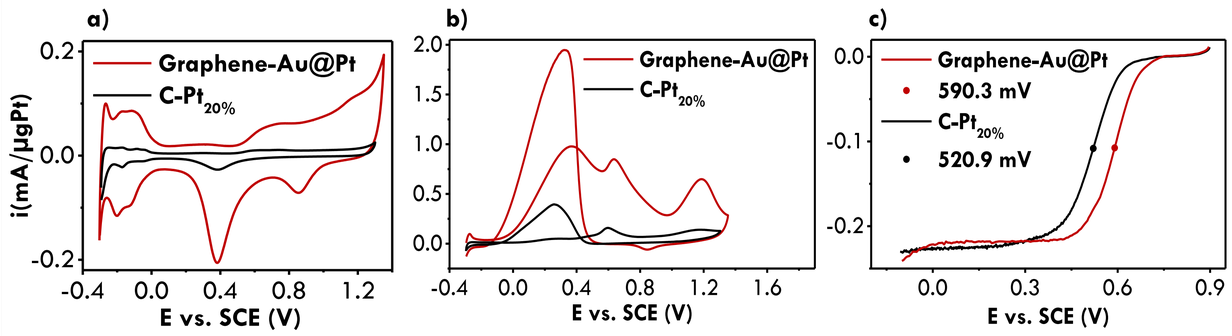


Fig. 4. Graphene-Au@Pt and C-$Pt_{20\%}$ electocatalysis: **a)** cyclic voltammograms in 0.1 M H_2SO_4 at 50 mV/s on glassy carbon electrodes (GCEs), **b)** electro-oxidation of 0.1 M FA (in 0.1 M H_2SO_4, 50 mV/s, on GCEs). **c)** ORR in 0.1 M $HClO_4$ (10 mV/s, on GC rotating disc electrode at 900 rpm).

PEMFC experiments:

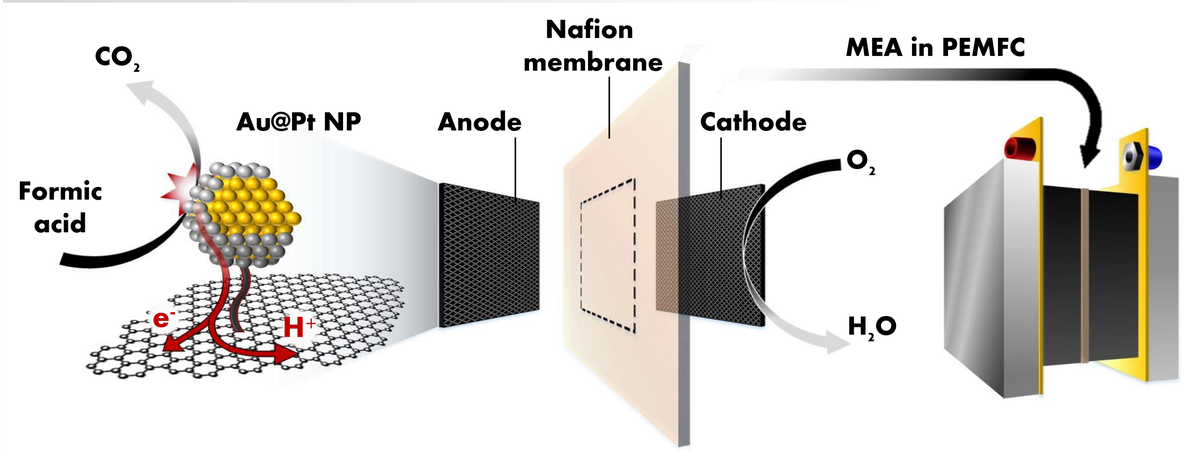


Fig. 5. Scheme of graphene-Au@Pt as anode catalyst in MEA.

Graphene-Au@Pt was tested as an anode catalyst in membrane electrode assembly (MEA) and compared to C-$Pt_{20\%}$. Commercial 1.0 mgPt/cm^2 was cathode catalyst in all experiments.

Experimental conditions:

Graphene-Au@Pt loading: 0.64 mgPt/cm^2,
C-$Pt_{20\%}$ loading: 0.68 mgPt/cm^2,
active area: 1.0 cm^2,
fuel flow: 2.0 mL/min,
O_2 flow: 100.0 mL/min,
temperatures used: 40, 60 and 80 °C.

The open circuit potential (OCP) for graphene-Au@Pt was 825 ± 9.9 mV and 728 ± 7.5 mV for C-$Pt_{20\%}$. The highest observed power output for graphene-Au@Pt was 122 ± 3.5 mW/cm^2 and 62 ± 3.2 mW/cm^2 for C-$Pt_{20\%}$ (Fig. 6) - average values of 5 graphene-Au@Pt and 4 C-$Pt_{20\%}$ measurements at 80 °C. Fig. 6. shows 96.8 % power increase for graphene-Au@Pt and 97 mV higher OCP than for C-$Pt_{20\%}$.

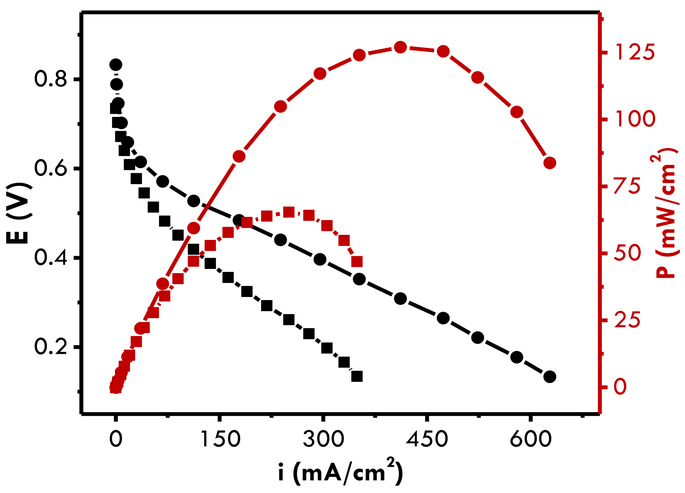


Fig. 6. Polarization (black) and power plots (red) of graphene-Au@Pt (-●-) and C-$Pt_{20\%}$ (-■-) at 80 °C.

Conclusions

1. Graphene-Au@Pt synthesis yielded atomically thin Pt shell, highly active for FA oxidation.
2. Chemical bonds between Au@Pt NPs and graphene improve stability.
3. FA oxidation on graphene-Au@Pt exhibits several times higher currents and 69.4 mV lower overpotential towards ORR than C-$Pt_{20\%}$.
4. Graphene-Au@Pt exhibits OCP of 825 ± 9.9 mV and 96.8 % higher power output (122 ± 3.5 mW/cm^2) than C-$Pt_{20\%}$ at 80 °C.

Graphene-Au@Pt is a Pt-efficient, highly active catalyst for FA oxidation in PEMFC application.

References

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2. C. Engelbrekt, N. Šešelj, R. Poreddy, A. Riisager, J. Ulstrup, J. Zhang, J. Mater. Chem. A, 4 (2016), 3, 3278-3286

Acknowledgement

Support from the Danish Council for Independent Research Technology and Production Sciences (DEF-1335-00330) is acknowledged.